Project 94987

Fission-Product Separation Based on Room-Temperature Ionic-Liquids

Hussey, Charles L.
University of Mississippi

RESULTS TO DATE: During the previous funding cycle for this project, we investigated the electrochemistry of Cs(I) in air and moisture-stable ionic liquids both with and without the addition of BOBCalixC6. These investigations revealed that the electrochemical windows of the dialkylimidazolium bis[(trifluoromethyl)sulfonyl]imide ionic liquids do not permit the direct electrochemical reduction of Cs(I), even when Hg electrodes are employed, because these organic cations are reduced at less negative potentials than Cs(I). However, Cs(I) coordinated by BOBCalixC6 can be electrolytically reduced to Cs(Hg) in tetraalkylammonium-based room-temperature ionic liquids such as tri-1-butylmethylammonium bis[(trifluoromethyl)sulfonyl]imide (Bu3MeN+Tf2N-) at Hg electrodes. Because this reduction process does not harm either the ionic liquid or the macrocycle, it is a promising method for recycling the cesium extraction system. The previous studies mentioned above were carried out under an inert atmosphere, i.e., in the absence of H2O and O2. However, it may not be economically feasible or even possible to carry out the recycling process in the absence of these contaminants during large-scale processing of aqueous tank waste. Thus, as described in our proposal, we have begun an investigation of the electrochemical recovery of Cs from the Bu3MeN+Tf2N- + BOBCalixC6 extraction system in an air atmosphere containing various amounts of water and oxygen. Our recent preliminary results were very surprising because they indicated that the electrochemical extraction process is relatively insensitive to the presence of small amounts of moisture even when the moisture content of the ionic liquid approaches 1000 ppm. Furthermore, we have found that the ?wet? ionic liquid can be easily dehydrated under reduced pressure or by sparging with dry nitrogen gas without the need for heat or any other specialized treatment. This implies that the electrochemical processing step following the chemical extraction of Cs(I) from tank waste can be carried out in an open cell, provided that the cell is blanketed with dry nitrogen gas. In a related investigation, we have examined another room-temperature ionic liquid for use in the extraction of Cs+ from aqueous tank waste. This ionic liquid, which is based on a cyclic aliphatic quaternary ammonium salt, 1-methyl-1-propylpiperidinium bis((trifluoromethyl)-sulfonyl)imide), exhibits lower viscosity and higher conductivity than Bu3MeN+Tf2N- and seems to be a promising candidate for our proposed application because it has been used successfully as an electrolyte in lithium batteries. We found that this ionic liquid is a better extraction solvent than Bu3MeN+Tf2N-.. That is, in conjunction with BOBCalixC6, the distribution coefficients for Cs(I) are much larger in the former than in the latter. Unfortunately, we have determined that this new ionic liquid is not stable toward Cs, and the electrochemical reduction of BOBCalixC62Cs(I) in this solvent was complicated by a reaction between the Cs(Hg) and the ionic liquid. This instability results in the production of black particulate matter and discoloration of the ionic liquid. In another investigation conducted with this DOE funding, we have examined the detailed mechanism of the electrochemical reduction of Cs(I) to Cs(Hg) at a mercury film electrode. The techniques used for this study included cyclic staircase voltammetry and chronopotentiometry. The Cs(Hg)x alloying reaction was found to exhibit three different phases. A manuscript describing these results is under preparation.

DELIVERABLES: Two articles describinbg this research are in preparation. A presentation is planned for the forthcoming Electrochemical Society Meeting in Los Angeles in October of 2005